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(54) A method for joining a fluorinated polymer cation exchange membrane

(57) A method is provided for joining a fluorinated polymer cation exchange membrane, which comprises interposing a porous hydrophilic fluorinated polymer film between a fluorinated polymer cation exchange membrane containing the pendent group of $-\text{COOA}$ (A represents H, R, NR_3H or NR_4 , wherein R is alkyl having 1 to 20 carbon atoms) on at least one side of the membrane and a fluorinated polymer cation exchange membrane or a fluorinated polymer film, then heat-pressing them. The invention markedly increases joining strength as compared with conventional methods.

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SPECIFICATION

A method for joining a fluorinated polymer cation exchange membrane

5 The present invention relates to a method for joining a fluorinated polymer cation exchange membrane. More specifically, the present invention relates to a method for joining a fluorinated polymer cation exchange membrane [X] containing the pendent group of -COOA on at least one side of the mem-
10 brane and a fluorinated polymer cation exchange membrane [Y] or a fluorinated polymer film. Hereinabove, A represents H, R, NR₃H or NR₄, in
15 which R is alkyl having 1 to 20 carbon atoms.

The joining of a cation exchange membrane is exceedingly useful in the industry. In the industrial utilization of the joining art of a cation exchange membrane, there are included, for example, forma-
20 tion of a cation exchange membrane in any desired shape, production of a sufficient size of the cation exchange membrane required for an industrial use when such a large size is difficult to be manufac-
25 tured. It is also useful in repairing a tear or a hole of the cation exchange membrane which occasionally took place during utilization or handling. The present invention provides a joining method of a fluorinated polymer cation exchange membrane which is very much useful industrially.

30 The joining method of the present invention is characterized by interposing a porous hydrophilic fluorinated polymer film between a cation exchange membrane [X] containing the pendent group of -COOA on at least one side of the membrane and a
35 cation exchange membrane [Y] or a fluorinated polymer film, then heat-pressing them.

A fluorinated polymer cation exchange membrane having carboxylic acid groups as the pendent group are well-known to the art as a capable membrane in
40 a wide use and the joining art of the membrane is extremely important.

A fluorinated polymer cation exchange membrane [X] used in the present invention may contain the pendent group of carboxylic acid groups on both
45 surfaces of the membrane, in the entirety of the membrane or the one surface of the membrane. The thickness of such carboxylic acid group layer is 1 μ or more, more preferably 10 μ or more.

The carboxylic acid groups include -COOH type, 50 -COOR, -COONR₃H or -COONR₄, which is obtained by the treatment of -COOH group with an alcohol, a tertiary amine, a quaternary ammonium base or a salt of the foregoing, respectively. Hereinabove, R represents alkyl having 1 to 20 carbon atoms. As
55 these treating agents, alcohols such as methanol, ethanol, etc., tertiary amines such as triethylamine etc., quaternary ammonium bases such as tetrabutylammonium hydroxide etc., may be employed. Salts of tertiary amines include triethylamine hydrochloride etc., and salts of quaternary ammonium bases
60 include tetrabutylammonium chloride etc.

A fluorinated polymer cation exchange membrane [X] is produced by polymerization of fluorocarbon monomers, or by denaturation of one or both sides
65 of a sulfonic acid type cation exchange membrane or

an ethylene diamine treated cation exchange membrane, sold by E.I. Du Pont de Nemours & Co.

A fluorocarbon polymer cation exchange mem-
brane [Y] may be identical with the cation exchange
70 membrane [X], or a fluorinated polymer cation exchange membrane having the pendent groups of sulfonic acid groups or sulfon amide groups, of which sulfonic acid groups or sulfon amide groups are treated with a tertiary amine, a quaternary
75 ammonium base or a salt of the foregoing. A cation exchange membrane having the pendent group of sulfonic acids includes "Nafion" #110, #315, #415 etc., produced and sold by E.I. Du Pont de Nemours & Company. A process for treatment of a cation
80 exchange membrane with the pendent groups of sulfonic acid groups with a quaternary ammonium base and the like is disclosed in the Japanese Patent Publication (non-examined) No. 49394/1975.

A fluorinated polymer film includes a film of a
85 polymer or a copolymer obtained by the polymerization of tetrafluoroethylene, 6-fluoropropylene, perfluoroalkylvinylether, 3-fluorochloroethylene and the like. For example, a copolymer of tetrafluoroethylene and 6-fluoropropylene and a polymer
90 of 3-fluorochloroethylene have melting points of 270°C and 215°C, respectively, and are preferably employed in particular, since their melting points are close to those of the cation exchange membranes.

A fluorinated polymer film is, prior to the joining,
95 subjected to hydrophilic treatment of at least, joined portion. The hydrophilic treatment is effected according to various processes, including the treatment by corona discharge. The hydrophilic treatment with activated sodium such as metallic
100 sodium, sodium dispersion, stabilized metallic sodium and the like is also effectively employed. The treatment with a surface active agent such as perfluorocarbon surface active agents and the like is also effective. Further, the hydrophilic treatment
105 with a titanium compound such as potassium titanate, titanium oxide and the like is also used.

A porous hydrophilic fluorinated polymer film includes a microporous membrane having the pendent groups of sulfonic acid groups or sulfon amide groups, of which sulfonic acid groups or sulfon
110 amide groups are treated with a tertiary amine, a quaternary ammonium base, or a salt of the foregoing, thereby being converted to the melt-processable membrane.

115 A porous fluorinated polymer film subjected to the hydrophilic treatment is also used as a porous hydrophilic fluorinated polymer film. Examples of the porous fluorinated polymer film is a porous film of polytetrafluoroethylene, which is exemplified by
120 "GORETEX" produced by JUNKOSHA K.K.

The hydrophilic treatment is carried out by corona discharge or by the treatment with an activated sodium such as metallic sodium, sodium dispersion, stabilized metallic sodium and the like. The treat-
125 ment with a surface active agent such as perfluorocarbon surface active agents, or a titanium compound such as potassium titanate, titanium oxide and the like is also effectively employed.

The joining is effected by heat-pressing. The
130 joining with adhesives, an alkanol solution dissolv-

ing a low equivalent weight cation exchange membrane, and the like are also available, but heat-pressing is the most effective. The heat-pressing is executed using a hot press and the like at 200 to 300°C, preferably 230 to 260°C. The pressing pressure is 2 to 150 kg/cm², preferably 10 to 100 kg/cm². The pressing time is 1 to 30 min., preferably 3 to 10 min.

It is not made clear why the joining strength can be markedly improved by the interposition of a porous hydrophilic fluorinated polymer film, followed by heat-pressing, but is surmised as below. That is, heat-melted resin of the cation exchange membrane, upon heat-pressing, penetrates into perforations of the porous fluorinated polymer film, then solidify in the perforations. By such, as it were, an "anchor-shaped" or "wedge-shaped" joining effect, a superior joining strength is provided as compared with a conventional method.

The present invention will be explained in more detail by way of examples that follow, which examples are not construed to limit the scope of the present invention.

Example 1

A carboxylic acid type cation exchange membrane, which was obtained by denaturizing both sides of a sulfonic acid type cation exchange membrane, was treated with hydrochloric acid to prepare a -COOH type membrane.

As a microporous membrane containing the pendent group of sulfonic acid groups, "Nafion" #701, produced by E.I. Du Pont de Nemours & Co, was treated with hydrochloric acid to give a -SO₃H type microporous membrane. The obtained microporous membrane was further treated for 1.5 hours with a 50 % aqueous methanol solution containing 0.2 mole of tetra(n-butyl)ammonium hydroxide.

Between two pieces of so treated -COOH type cation exchange membranes, was the so treated microporous membrane sandwiched, then heat-pressed for 5 min. at 250°C under the pressure of 70 kg/cm². The resulting joined membranes were immersed in a depleted brine removed from an ion exchange membrane electrolytic cell for 2 months, but no peeling off of the joined portion was observed.

Example 2

A carboxylic acid type cation exchange membrane obtained by denaturation of one side of a sulfonic acid type cation exchange membrane was treated with hydrochloric acid, then a -COOH type cation exchange membrane [X] being obtained.

A microporous membrane containing the pendent group of sulfonic acid groups, "Nafion" #710 was subjected to the treatment with hydrochloric acid to obtain a -SO₃H type. The -SO₃H type microporous membrane was then treated for 1.5 hours with a 50 % aqueous methanol solution containing 0.2 mole of tetra (n-butyl)ammonium hydroxide.

A cation exchange membrane with the pendent group of sulfonic acid groups, "Nafion" #315, produced by E.I. Du Pont de Nemours & Company was converted to a -SO₃Na type membrane with

sodium hydroxide. The obtained -SO₃Na type membrane was then treated for 1 hour with a 50% aqueous methanol solution containing 0.2 mole of tetra(n-butyl)ammonium chloride to provide thus treated cation exchange membrane [Y].

Between the so treated cation exchange membrane [X] and the so treated cation exchange membrane [Y], the so treated microporous membrane was sandwiched, then heat-pressed for 7 min. at 240°C under the pressure of 80 kg/cm². The joined membranes were subjected to the immersion test for 2 months in a similar fashion to that of Example 1. No peeling off of the joined portion occurred even after 2 months.

Example 3

Both sides of a sulfonic acid type cation exchange membrane were denaturized to obtain a carboxylic acid type membrane, then treated with hydrochloric acid, thereby preparing a -COOH type membrane. The obtained membrane was further treated for 16 hours with a 50% aqueous methanol solution containing 0.2 mole of tetra(n-butyl)ammonium hydroxide. The heat-pressing was followed similarly to that of Example 1. The resultant joined membranes were immersed for 2 months in a depleted brine exiting from an ion exchange membrane electrolytic cell, but peeling off of the joined portion was not seen.

Example 4

A carboxylic acid type exchange membrane, obtained by denaturation of both sides of a sulfonic acid type cation exchange membrane, was converted to a -COOH type membrane by the treatment with hydrochloric acid.

On the other hand, "Nafion" #701, a microporous membrane containing the pendent group of sulfonic acid groups, which was produced by E.I. Du Pont de Nemours & Company was treated in a similar manner to that of Example 1.

A film of copolymer of tetrafluoroethylene and 6-fluoropropylene was subjected to corona discharge on its one side.

The joined membrane and film resulted from heat-pressing at 270°C under the pressure of 70 kg/cm² were immersed for 2 months in a depleted brine discharged from an ion exchange membrane electrolytic cell, no peeling off of the joined portion was observed.

Example 5

A carboxylic acid type cation exchange membrane was prepared by denaturizing both sides of a sulfonic acid type cation exchange membrane, then converted to a -COOH type membrane by the treatment with hydrochloric acid.

As a porous hydrophilic fluorinated polymer film, a film of polytetrafluoroethylene whose porous one side was subjected to corona discharge was employed.

The joined membranes heat-pressed in a similar manner to that of Example 4 were immersed for 2 months in a depleted brine removed from an electrolytic cell of an ion exchange membrane, but no peeling off took place.

Example 6

A carboxylic acid type cation exchange membrane obtained by denaturizing both sides of a sulfonic acid type cation exchange membrane was converted to a -COOH type membrane by the treatment with hydrochloric acid.

A porous film of polytetrafluoroethylene, both sides of which were treated by corona discharge was used as a porous hydrophilic fluorinated polymer film.

A film of copolymer of tetrafluoroethylene and 6-fluoropropylene was treated by corona discharge in its one side.

The membrane and the film treated above, respectively, were heat-pressed similarly to Example 4 with the interposition of the treated porous hydrophilic fluorinated polymer film. The joined membrane and film were subjected to the immersion test for 2 months in a depleted brine exiting from an ion exchange membrane electrolytic cell, but no peeling off of the joined portion was observed.

CLAIMS

1. A method for joining a fluorinated polymer cation exchange membrane, which comprises interposing a porous hydrophilic fluorinated polymer film between a fluorinated polymer cation exchange membrane [X] containing the pendent group of -COOH (A represents H, R, NR_3H or NR_4 , wherein R is alkyl having 1 to 20 carbon atoms) on at least one side of the membrane and a fluorinated polymer cation exchange membrane [Y] or a fluorinated polymer film, then heat-pressing them.

2. The method of Claim 1, wherein said porous hydrophilic fluorinated polymer film comprises a microporous membrane containing pendent groups of sulfonic acid groups or sulfon amide groups, whose sulfonic acid groups or sulfon amide groups are treated with a tertiary amine, a quaternary ammonium base, or a salt of the foregoing amine or base.

3. The method of Claim 1, wherein said porous hydrophilic fluorinated polymer film comprises a porous hydrophilic fluorinated polymer film subjected to hydrophilic treatment by corona discharge, or with metallic sodium, sodium dispersion, stabilized metallic sodium, potassium titanate, titanium oxide or surface active agents.

4. The method of Claim 1, wherein said fluorinated polymer cation exchange membrane [Y] comprises the fluorinated polymer cation exchange membrane [X].

5. The method of Claim 1, wherein said fluorinated polymer cation exchange membrane [Y] comprises a fluorinated polymer cation exchange membrane containing pendent groups of sulfonic acid groups or sulfon amide groups, whose sulfonic acid groups or sulfon amide groups are treated with a tertiary amine, a quaternary ammonium base, or a salt of the foregoing amine or base.

6. The method of Claim 1, wherein said fluorinated polymer film comprises a fluorinated polymer film subjected to hydrophilic treatment by corona discharge, or with metallic sodium, sodium disper-

sion, stabilized metallic sodium, potassium titanate, titanium oxide or surface active agents.

7. A method for joining a fluorinated polymer cation exchange membrane substantially as described with reference to any one of the examples herein.

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